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IN REPLY REFER TO:

Attorney Docket No. 82602

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The below identified patent application is available for licensing. Requests for information should be addressed to:

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NON-CHROMATE CONVERSION COATINGS

TO WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) WAYNE C. TUCKER, and (2) MARIA G. MEDEIROS, employees of the United States Government, citizens of the United States of America, and (3) RICHARD BROWN, citizen of the United Kingdom and residents of (1) Exeter, County of Washington, State of Rhode Island, (2) Bristol, County of Bristol, State of Rhode Island, (3) Wakefield, Washington County, Rhode Island have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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PATENT TRADEMARK OFFICE

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3 STATEMENT OF GOVERNMENT INTEREST

4 The invention described herein may be manufactured and used
5 by or for the Government of the United States of America for
6 Governmental purposes without the payment of any royalty thereon
7 or therefor.

8

9 CROSS REFERENCE TO OTHER PATENT APPLICATIONS

10 This patent application is co-pending with one related
11 patent applications entitled NON-CHROMATE METAL SURFACE ETCHING
12 SOLUTIONS (Attorney Docket No. 82602), by the same inventors as
13 this application.

14

15 BACKGROUND OF THE INVENTION

16 (1) FIELD OF THE INVENTION

17 The present invention relates to a non-chromate conversion
18 coating and method of treating a metal surface with same, and
19 more particularly, to a "drop-in replacement," such as a
20 titanate, for a chromate in a conventional conversion coating
21 solution that otherwise would contain the chromate.

22 (2) DESCRIPTION OF THE PRIOR ART

23 It is known that solutions containing hexavalent chromium
24 can be used to treat the surface of a metal, such as aluminum, to
25 effectively keep the metal surface from rusting. However,

1 although hexavalent chromium is an efficient rust-proofing agent,
2 it is highly toxic and adversely affects the environment and
3 human health. For this reason, many chromate-free chemical
4 conversion coatings for metal surfaces have been proposed.

5 Thus, various non-chromate conversion coatings, such as the
6 conversion coatings described in Tomlinson U.S. Patent No.
7 5,759,244, the disclosure of which is incorporated by reference
8 herein, have been disclosed which are designed to render a metal
9 less reactive in a corrosive environment. Such non-reactive or
10 less reactive metal surfaces produce a corrosion resistant outer
11 layer on the base metal or its oxide thereby leaving the
12 underlying metal protected from the environment. These coatings
13 are applied in one or more stages and are subsequently rinsed
14 with water to remove undesirable contaminants.

15 Chromate-free conversion coatings are therefore generally
16 based on chemical mixtures that react with a metal substrate
17 surface to form a protective layer. Many of these conversion
18 coatings are based on Group IV-B metals such as titanium,
19 zirconium and hafnium. For example, U.S. Patent No. 5,743,971 to
20 Inoue et al discloses a rust proof film-forming composition for
21 treating a metal surface comprising an oxidated substance, a
22 silicate and/or silicone dioxide and at least one member selected
23 from the group consisting of metal cations of titanium,
24 zirconium, cerium, strontium, vanadium, tungsten, and molybdenum.
25 A metal substrate is provided a rust proof film by immersing it

1 in the foregoing liquid rust proof film-forming composition.
2 Similarly, U.S. Patent No. 5,855,695 to McMillen et al discloses
3 a non-chrome passivating composition employed as a post-rinse for
4 enhancing the corrosion resistance of phosphated metal
5 substrates. The composition comprises the reaction product of an
6 epoxy-functional material containing at least two epoxy groups
7 and an alkanolamine, or a mixture of alkanolamines. The non-
8 chrome passivating composition further comprises a Group IV-B
9 metal ion, or a mixture of Group IV-B metal ions. Moreover, U.S.
10 Patent No. 5,897,716 to Reghi et al discloses a chemically and
11 thermally stable chromate-free aqueous liquid treatment for
12 metals for imparting corrosion resistance thereto. The chromate-
13 free aqueous liquid comprises components selected from the group
14 consisting of H_2TiF_6 , H_2ZrF_6 , H_2HfF_6 , H_2SiF_6 , H_2GeF_6 , H_2SnF_6 , HBf_4
15 and mixtures thereof.

16 The shortcoming of conventional non-chromate conversion
17 coatings, such as those described above, is that they cannot be
18 integrated into and employed in place of chromates in current
19 metal treatment coatings which employ chromates. As such,
20 conventional non-chromate conversion coatings are usually
21 sufficiently different from previously employed chromate-
22 containing conversion coatings that significant changes are
23 required to be made in the metal treating process and in the
24 production of the conversion coating itself. These changes can
25 amount to substantial expenditures and usually require additional

1 approvals from the Department of the Navy or a regulatory agency
2 of the United States Government. Thus, there is a need for a
3 "drop-in replacement" that can be employed in place of chromate
4 compounds, such as sodium dichromate, now used in conventional
5 chromate conversion coatings. "Drop-in replacement" refers to a
6 compound that can be employed in a conventional conversion
7 coating in lieu or in place of a chromate without requiring any
8 or substantial changes in the make-up of the conversion coating
9 or its substituents.

10
11 SUMMARY OF THE INVENTION

12 It is a primary object of the present invention to provide a
13 non-chromate conversion coating for treating metals which
14 contains a titanate in place of a chromate.

15 It is a further primary object of the invention to provide a
16 "drop-in replacement" for a chromate that can be employed in a
17 conversion coating which otherwise would employ a chromate.

18 It is a further primary object of the invention to provide a
19 method of rust-proofing a metal substrate by applying a non-
20 chromate titanate conversion coating thereto.

21 Another object of the invention is to provide a one-stage
22 method of rust proofing a metal substrate by applying a non-
23 chromate titanate conversion coating thereto including sodium
24 metatinate and/or potassium titanate.

1 Another object of the invention is to provide a non-chromate
2 conversion coating that excludes therein organic additives,
3 structural component additives or chelating agents.

4 The objects of the invention are accomplished by providing a
5 highly effective, non-chromate conversion coating which includes
6 a titanate, such as sodium metatitanate or potassium titanate, in
7 lieu of a chromate in a typical conversion coating that otherwise
8 would contain a chromate.

9 The present invention is developed on the basis of findings
10 that an excellent rust proof film can be obtained by immersing a
11 metal substrate in an aqueous solution which includes sodium
12 dichromate, sodium fluoride, potassium ferricyanide and nitric
13 acid in an amount to provide a pH of 1.2 to 2.2. It is believed
14 that the chromate provides corrosion protection by way of a
15 cathodic reaction, specifically, the reduction of oxygen in the
16 presence of water:



18 This cathodic reaction is similar for many systems, and by
19 changing the oxygen concentration in the solution, reveals the
20 cathodic behavior of the chromate. Moreover, when the reduction
21 of oxygen is the rate controlling reaction and chromates are
22 present, other metals and lower oxygen levels show similar
23 behavior, that is a lower or decreased limiting current density.

24 Test results show that a metal tested without a conversion
25 coating has a high limiting cathodic density. For example,

1 untreated Al2024T3 has a limiting cathodic current density of 10-
2 20 A/cm², however, when a chromate conversion coating is applied,
3 the cathodic limiting current density is lowered to 3-7 A/cm².
4 However, since personal exposure limits (PEL) for chromates is
5 0.1 mg/m³ (milligram per cubic meter), chromate containing
6 conversion coatings are not practical for use. Thus, a "drop-in
7 replacement" for the chromate in the chromate-containing
8 conversion coating is highly desired.

9 Sodium metatitanate and potassium titanate have been found
10 to be well suited as "drop-in replacements" for chromates in
11 conversion coatings which, in addition to sodium dichromate,
12 contain sodium fluoride, potassium ferricyanide and nitric acid.
13 For example, test results show that a conversion coating which
14 includes a "drop-in replacement" according to this invention in
15 place of a chromate produces a metal surface having a cathodic
16 limiting current density of 0.5 to 1 A/cm³. Furthermore, the PEL
17 for such a conversion coating is 15 mg/m³. Thus, the present
18 invention provides a highly effective, non-toxic conversion
19 coating which otherwise would include toxic chromate compounds,
20 such as sodium dichromate.

22 DESCRIPTION OF THE PREFERRED EMBODIMENT

23 The present invention will hereafter be described in detail
24 with reference to the following embodiments.

1 The preferred embodiment of the present invention comprises
2 a non-chromate conversion coating for providing corrosion
3 resistance to metals which includes sodium metatitanate and/or
4 potassium titanate in a conversion coating that otherwise would
5 contain a chromate. The preferred embodiment further includes a
6 method of rust proofing a metal which employs the non-chromate
7 conversion coating of the present invention.

8 A typical chromate-containing conversion coating employed in
9 a metal treatment process includes sodium dichromate, sodium
10 fluoride, potassium ferricyanide and nitric acid, and more
11 particularly, about 0.025 M (molecular weight in grams per one
12 liter of solvent) sodium dichromate, about 0.024 M sodium
13 fluoride, about 0.015 M potassium ferricyanide and an amount of
14 nitric acid to provide a pH of 1.2 to 2.2. The present invention
15 provides a means of replacing this toxic metal treating solution
16 with a similar, non-toxic variant that includes the original non-
17 chromate constituents and thus, can be easily substituted for the
18 chromate-containing solution and employed in the same metal
19 treating process. Therefore, the preferred embodiment of the
20 present invention provides a conversion coating comprising sodium
21 metatitanate, sodium fluoride, potassium ferricyanide and an
22 amount of nitric acid to provide a pH of about 1.0 to about 6.0.
23 More particularly, the conversion coating of the present
24 invention comprises a solution of about 0-1 M sodium
25 metatitanate, about 0-1 M sodium fluoride, about 0-1 M potassium

1 ferricyanide and a balance of nitric acid to adjust the pH to
2 about 1.0 to about 6.0. Alternatively, potassium titanate can be
3 employed in place of sodium metatitanate. In that case, the
4 conversion coating comprises potassium titanate in an amount
5 ranging from about 4 g/l (grams per liter) to about 8 g/l, sodium
6 fluoride in an amount ranging from about 2 g/l to about 6 g/l and
7 nitric acid to adjust the pH to a range of about 1.0 to about
8 6.0.

9 Since the conversion coatings of the present invention are
10 drop-in-replacement compositions, additional additives, including
11 organic additives, structural component additives or chelating
12 agents for keeping the metals therein in solution are not needed.
13 Preferably, therefore, no such additives are included in the
14 compositions.

15 To provide corrosive resistance to a metal surface by way of
16 the foregoing conversion coatings, the metal surface must first
17 be washed with a solvent, such as methanol or TCE
18 (trichloroethylene) in order to solvent wipe. Thereafter, the
19 surface is degreased with a 2% sodium hydroxide solution or any
20 other suitable degreaser such as a caustic solution for about one
21 minute, at about 50-60° C. Next, the metal surface is rinsed
22 with deionized water to remove any degreaser or solvent on the
23 metal's surface before being immersed in a deoxidizing solution
24 such as SMUTGO®. The metal surface is immersed therein for ten
25 minutes at about room temperature thereby deoxidizing the metal's

1 surface. Thereafter, the metal surface is again rinsed with
2 deionized water to remove any deoxidizing solution on its surface
3 before the non-chromate conversion coating of the present
4 invention is applied. It is preferred that the conversion
5 coating be around about 60-80° C during application. Lastly, the
6 metal is rinsed in a deionized water and allowed to air dry. An
7 advantage of the present method is that the non-chromate
8 conversion coating herein has only to be applied once to the
9 metal substrate, thus, the present method is a one-stage process.
10 Prior art non-chromate coatings and methods of applying same can
11 require multiple applications. Further, by rinsing the metal
12 surface following applying the present conversion coating, a dry-
13 on polymer surface coating is not disposed on the metal surface
14 as is the case with prior art coatings.

15 A metal substrate, such as aluminum, that undergoes the
16 foregoing treatment is provided a lower cathodic limiting current
17 density than if allowed to go untreated. Specifically, test
18 results show that application of the non-chromate conversion
19 coating of the present invention to Al2024T3 results in a
20 cathodic limiting current density of 0.5 to 1 A/cm². Test
21 results were attained using a salt spray test over ten days.

22 While the preferred embodiment of the non-chromate
23 conversion coating and method of applying same has been described
24 in detail above, various modifications and variations of the
25 invention are possible in light of the above teachings. For

1 example, boric acid can be employed in place of nitric acid to
2 adjust the pH of the conversion coating. It is therefore
3 understood that within the scope of the appended claims the
4 invention may be practiced otherwise than above-described.

2
3 NON-CHROMATE CONVERSION COATINGS

4
5 ABSTRACT OF THE DISCLOSURE

6 A non-chromate conversion coating and method of
7 applying same wherein the coating comprises a titanate, such as
8 potassium titanate or sodium metatitanate, as a "drop-in
9 replacement" for a chromate in an otherwise chromate-containing
10 conversion coating.